



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/EP93/02559 (22) International Filing Date: 20 September 1993 (20.09.93) (30) Priority data: 92202964.0 25 September 1992 (25.09.92) EP <i>(34) Countries for which the regional or international application was filed:</i> NL et al. (71) Applicant (for AU BB CA GB IE LK MN MW NZ SD only): UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4 4BQ (GB). (71) Applicant (for all designated States except AU BB CA GB IE LK MN MW NZ SD US): UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).		(72) Inventors ; and (75) Inventors/Applicants (for US only) : HAVERKAMP, Johan [NL/NL]; de Kroeskarper 40, NL-2661 KL Bergschenhoek (NL). VAN DER VLIST, Pieter [NL/NL]; Tarwestraat 5, NL-2989 AV Ridderkerk (NL). WARMOESKERKEN, Marinus, Maria, C., G. [NL/NL]; Oostsingel 204, NL-2612 HL Delft (NL). WILLEMSE, Simon [NL/NL]; Surinamesingel 31, NL-3131 XL Vlaardingen (NL). (74) Agent: KAN, Jacob, H.; Unilever N.V., Patent Division, P.O. Box 137, NL-3130 AC Vlaardingen (NL). (81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: CLEANING PROCESS (57) Abstract A process for cleaning articles whereby soiled articles are immersed in an enzymatic aqueous cleaning medium and radiated with ultrasonic energy, characterized in that the enzymatic aqueous cleaning medium contains an enzyme having lipolytic activity.		

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CLEANING PROCESSTECHNICAL FIELD

This invention relates to a cleaning process, and more in particular to a process for cleaning soiled articles such as fabrics, using an ultrasonic energy source. In particular, the invention relates to a process whereby soiled articles are immersed in an enzymatic aqueous cleaning medium and radiated with ultrasonic energy.

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BACKGROUND AND PRIOR ART

Cleaning processes whereby ultrasonic energy is used have been known in the art for many years. In such a process, the articles to be cleaned are immersed in an aqueous cleaning medium and are radiated with ultrasonic energy. In particular, numerous publications relate to ultrasonic fabric washing processes. For that purpose, the aqueous cleaning medium usually contains one or more conventional ingredients of detergent products such as surfactants, builders and the like. EP-A-258 816 (Henkel) discloses a ultrasonic fabric washing process wherein the wash load is treated with a cleaning medium having such a strong wetting capacity that the wash load is thoroughly wetted and de-aerated.

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It is also been suggested to incorporate enzymes in products for ultrasonic fabric washing. For example, EP-A-258 816 (Henkel) suggests the use of an enzymatic aqueous medium in an ultrasonic fabric washing process. Suitable enzymes are in particular alkaline proteases. It is shown that the presence of an alkaline protease in the wash liquor has a beneficial effect on the cleaning performance of the detergent product in an ultrasonic washing process. It is mentioned but not exemplified that amylases, lipases, pectinases, nucleases and/or oxydoreductases can also be used.

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Furthermore, JP-A-01026779 (Kao) discloses an ultrasonic fabric washing process whereby the cleaning solution contains a cellulase enzyme.

- 5 In his article in Chemistry and Industry 1990, pages 183-186, Malmos notes that it is known that generally the activity of lipases during a conventional washing process is low, and Lipolase (Trade mark of Novo/Nordisk) is no exception. During the drying process, when the water
10 content of the fabric is reduced, any remaining enzyme regains its activity and the fatty stains are hydrolysed. During the following wash cycle the hydrolysed material is removed. This also explains why the effect of lipases is low after the first washing cycle, but significant in the
15 following cycles.

- In view of these more recent findings, one skilled in the art would hardly expect any benefits from the presence of an enzyme having lipolytic activity in an ultrasonic
20 washing process, especially when considering the short contact time which is in the order of minutes.

- Contrary to what one would expect, we have now surprisingly found that the incorporation of an enzyme having lipolytic
25 activity into the aqueous cleaning medium of an ultrasonic washing process leads to a significant improvement of the wash performance.

DEFINITION OF THE INVENTION

- 30 According to the invention, there is provided a process for cleaning articles whereby soiled articles are immersed in an enzymatic aqueous cleaning medium and radiated with ultrasonic energy, characterised in that the enzymatic aqueous cleaning medium contains an enzyme having lipolytic
35 activity of 0.1 to 500 LU/ml. Preferably, the soiled articles are fabrics. Preferably, the cleaning medium comprises surface active agents.

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DESCRIPTION OF THE INVENTION

In the process of the present invention, soiled articles such as fabrics are immersed in an enzymatic aqueous cleaning medium and radiated with ultrasonic energy.

- 5 The principles of ultrasonic washing are well known in the art and can, for instance, be derived from the earlier mentioned EP-A-258 816 (Henkel). For the purpose of this application we define ultrasonic energy as usually involving frequencies of about 10 kilo Hertz (kHz) to about
10 100 kHz, however, higher frequencies of up to 10 mega Hertz (MHz) may also be used. In general, ultrasonic energy will be applied to the enzymatic aqueous cleaning medium for about 15 minutes or less, preferably between 0.25 to 10 minutes and more preferably between 0.5 to 5 minutes.
15 Optionally, the wash load may be agitated slowly, preferably during "pulsing periods", i.e. periods in which no ultrasonic energy is applied to the wash load.

- The enzymatic aqueous cleaning medium used in the present
20 process comprises 0.05 to 50 g/l, preferably 0.1 to 10 g/l (most preferably up to 5 g/l) of a conventional detergent composition, which includes conventional detergent ingredients such as surface active agents, builders, etc..

- 25 The surface active agents may be chosen from the surfactants described "Surface Active Agents" Vol. 1, by Schwartz & Perry, Interscience 1949, Vol. 2 by Schwartz, Perry & Berch, Interscience 1958, in the current edition of "McCutcheon's Emulsifiers and Detergents" published by
30 Manufacturing Confectioners Company or in "Tenside-Taschenbuch", H. Stache, 2nd Edn., Carl Hauser Verlag, 1981. The surfactants preferably comprise one or more nonionic and/or anionic surfactants. They may also comprise amphoteric or zwitterionic detergent compounds, but this is
35 not normally desired owing to their relatively high cost.

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Suitable nonionic detergent compounds which may be used include, in particular, the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example, aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide either alone or with propylene oxide. Specific nonionic detergent compounds are C₆-C₂₂ alkyl phenol-ethylene oxide condensates, generally 5 to 25 EO, i.e. 5 to 25 units of ethylene oxide per molecule, and the condensation products of aliphatic C₈-C₁₈ primary or secondary linear or branched alcohols with ethylene oxide, generally 5 to 10 EO. Other examples of suitable nonionic surfactants are alkyl polyglycosides and polyhydroxy fatty acid amide surfactants such as disclosed in WO-A-92/06154 (Procter & Gamble).

Suitable anionic detergent compounds which may be used are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher C₈-C₁₈ alcohols, produced for example from tallow or coconut oil, sodium and potassium alkyl C₉-C₂₀ benzene sulphonates, particularly sodium linear secondary alkyl C₁₀-C₁₅ benzene sulphonates; and sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum. The preferred anionic detergent compounds are sodium C₁₂-C₁₈ alkyl sulphates owing to their favourable compatibility with lipolytic enzymes.

Surface active agents may preferably be present in amounts of from 0.1% by weight of the composition, more preferably 0.5% by weight and preferably up to 70% by weight, more preferably up to 60% by weight of the composition. For use

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in fabric washing the level of surface active agents is preferably from 5% by weight, more preferably from 10% by weight and preferably up to 60 % by weight, more preferably up to 40 % by weight, most preferably up to 35% by weight.

- 5 For use in the mechanical washing of dishes the level of surface active agents is preferably from 0.5% by weight to amounts to about 60% by weight depending upon their type and properties. Preferably low-to non-foaming nonionic surfactant are used in properly built or highly built
- 10 compositions in amounts to 7% by weight. Higher levels of highly deterative surfactants, i.e. up to 70% by weight, preferably 60% by weight, may be used in lower builder containing active/enzyme-based compositions.
- 15 Preferably the concentration of surface active agents in the wash liquor is from 0.001 to 20 g/l, preferably from 0.05 to 10 g/l, most preferably up to 5 g/l.

- The enzymatic detergent composition used in the present
- 20 invention may further contain from 5 to 60%, preferably from 20 to 50% by weight of a detergency builder. This, detergency builder may be any material capable of reducing the level of free calcium ions in the wash liquor and will preferably provide the composition with other beneficial
- 25 properties such as an alkaline pH, the suspension of soil removed from the fabric and the suspension of the fabric-softening clay material.

- Examples of suitable detergency builders include
- 30 precipitating builders such as the alkali metal carbonates, bicarbonates, orthophosphates, sequestering builders such as the alkali metal tripolyphosphates or nitrilotriacetates, or ion exchange builders such as the amorphous alkali metal aluminosilicates or the zeolites.

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The characteristic feature of the process of the present invention is that an enzyme having lipolytic activity is

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used in the ultrasonic cleaning process. In principle, any enzyme having sufficient lipolytic activity may be used in the process. Preferably a lipase derived from micro-organisms are used, more preferably a bacterial or fungal lipase. Most preferably the enzyme having lipolytic activity is selected from Thermomyces lipases or variants thereof, cutinases or variants thereof, Pseudomonas lipases or variants thereof, Fusarium lipases or variants thereof and/or Chromobacter lipases or variants thereof.

10

There are various publications on lipolytic enzymes or lipases. For example, EP-A-214 761 (Novo/Nordisk) gives detailed description of lipases derived from organisms of the species Pseudomonas cepacia, and certain uses therefor. EP-A-258 068 (Novo/Nordisk) gives detailed description of lipases derived from organisms of the genus Thermomyces (previous name Humicola) and certain uses therefor.

15

Examples of known lipase-containing detergent compositions are provided by EP-A-205 208 and EP-A-206 390 (Unilever) which relate to a class of lipases defined on the basis of their immunological relationships, and describe their use in detergent compositions and textile washing. The preferred lipases are those derived from P. fluorescens, P. gladioli and Chromobacter species.

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EP-A-331 376 (Amano) describes lipases and their production by rDNA technique, and their use, including an amino acid sequence of lipase from Pseudomonas cepacia. Further lipase enzymes produced by rDNA technique are described in for example WO-A-89/09263 (Gist-Brocades) and EP-A-218 272 (Gist-Brocades).

30

In spite of the large number of publications on lipase enzymes and their modifications, only the lipase from Humicola lanuginosa has so far found wide-spread commercial

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application as additive for fabric washing products. It is available from Novo/Nordisk under the trade name Lipolase®.

Other lipases that can be used in the present invention are
5 lipases derived from Pseudomonas pseudoalcaligenes and variants thereof, e.g. Liponax®, and lipases derived from Pseudomonaas putida and variants thereof, e.g. Lumafast®.

Furthermore, it should be noted that there are a number of
10 publications describing various hydrolase enzymes which are also capable of hydrolysing mono-, di-, or triglycerides. For example, WO-A-90/09447 (Plant Genetics Systems) discloses a cutinase enzyme from Fusarium solani pisi which is capable of hydrolysing triolein. Because there appears
15 to be some confusion with regard to the nomenclature of these enzymes, we define an enzyme having lipolytic activity for the purposes of this patent application as any enzyme capable of hydrolysing mono-, di-, or triglycerides. The cutinase gene from Fusarium solani pisi has been cloned
20 and sequenced (Ettinger et al., (1987) Biochemistry 26, 7883-7892). WO-A-90/09446 (Plant Genetics Systems) describes the cloning and production of this gene in E. coli.

25 The present invention also provides a number of combinations of the enzyme having lipolytic activity and further, conventional constituents used in detergent systems, to provide useful advantage in the ultrasonic removal of fatty material and material adsorbed to the
30 fatty material in soil on textile.

The other components of such detergent compositions can be of any of many known kinds, for example as described in GB-A-1 372 034 (Unilever), US-A-3 950 277, US-A-4 011 169 and
35 EP-A-179 533 (Procter & Gamble), EP-A-205 208 and EP-A-206 390 (Unilever), JP-A-63-078000 (Lion), and Research Disclosure 29056 of June 1988. In several useful

embodiments the detergent compositions can be formulated as described in EP-A-407 225.

- The enzyme having lipolytic activity can usefully be added
5 to the detergent composition in the form of a granular composition, a solution or a slurry of lipolytic enzyme with carrier material (e.g. as in EP-A-258 068 and Savinase® and Lipolase® products of Novo/Nordisk).
- 10 The amount of enzyme having lipolytic activity can be chosen within wide limits. Preferably, the enzymatic aqueous cleaning medium contains 0.1 to 500 LU/ml. It is especially preferred to use about 0.5 to 50 LU/ml. In this
15 specification lipase units are defined as they are in EP-A-258 068 (Novo/Nordisk). Similar considerations apply mutatis mutandis in the case of other enzymes, which may also be present.

- Advantage may be gained in such detergent compositions,
20 where protease is present together with the enzyme having lipolytic activity, by selecting such protease from those having pI lower than 10. EP-A-271 154 (Unilever) describes a number of such proteases. Proteases for use together with lipolytic enzyme may include subtilisin of for example BPN'
25 type or of some of the other types of subtilisin disclosed in the literature, some of which have already been proposed for detergents use, e.g. mutant proteases as described in for example EP-A-130 756 (Genentech), US-A-4 760 025 (Genencor), EP-A-214 435 (Henkel), WO-A-87/04661 (Amgen),
30 WO-A-87/05050 (Genex), Thomas et al. (1986) in Nature 5, 316, and 375-376 and in J.Mol.Biol. (1987) 193, 803-813, Russel et al. (1987) in Nature 328, 496-500, and others.

- WO-A-92/08779 (Procter & Gamble) discloses liquid detergent
35 compositions comprising a lipase and a modified bacterial serine protease, which is said to be more compatible with the lipase. The proteases are modified in that the

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methionine adjacent to the active-site serine has been replaced by another amino acid.

The formulation of detergent compositions according to the
5 invention can be further illustrated by reference to the Examples D1 to D14 of EP-A-407 225 (Unilever).

It should be pointed out here that the cleaning process of the present invention is not only suitable for cleaning
10 fabrics, but the principle of the invention can also be applied in the cleaning of other soiled objects such as dishes and/or other table ware, or medical equipment.

The invention is now further and non-limitatively
15 illustrated in the following Examples. The experimental setup is shown in Figure 1.

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EXAMPLE 1

The following wash experiments were performed in a standard Tergotometer containing 1 l of tap water (9° German Hardness). Eight EMPA 101 (ex Eidgenössische Material-
 5 prüfungsanstalt St. Gallen, Switzerland) test cloths of 7 x 7 cm were washed for 10 minutes at a temperature of 30°C, at an agitator speed of 100 rpm. The ultrasonic energy was supplied by a Branson ultrasonic probe having a tip of 1/8" with a mean power of 38 Watt. The operating frequency was
 10 23 kHz. The experimental setup is shown in Figure 1. The wash liquor contained 3 g/l of a detergent product having the following composition (in % by weight):

	Dodecyl Benzene Sulphonate	11.2
15	Ethoxylated alcohol nonionic surfactant 7 EO	4.6
	Soap (pristerine 4950)	1.0
	Sodium tripolyphosphate	39.5
	Sodium carbonate	3.9
	Sodium silicate	7.3
20	Sodium carboxymethyl cellulose	0.6
	Fluorescer	0.2
	Sodium sulphate	31.7
	Water	rest

25 After the washing, the reflectance at 460 nm was used to monitor the cleaning action. The results are shown in the Table. It is clear that the lipase effect, which is the difference between the reflectance at 460 nm after the ultrasonic wash in the presence and in the absence of
 30 lipase, increases with the lipase concentration.

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EXAMPLE 2

Example 1 was repeated using the following detergent product at 2.6 g/l:

5	Dodecyl Benzene Sulphonate	8.0
	Ethoxylated alcohol nonionic surfactant 12 EO	1.8
	Ethoxylated alcohol nonionic surfactant 6 EO	0.7
	Ethoxylated alcohol nonionic surfactant 7 EO	2.2
	Alf5	0.8
10	Zeolite	42.0
	Acrylic/Maleic copolymer (CP5 ex BASF)	4.0
	Sodium silicate	1.0
	Calcium Dequest	0.3
	Sodium sulphate	18.0
15	Water and minors	12.6

The cleaning results are shown in the Table. It can be seen that the lipase effect for this phosphate-free formulation is significantly better than for the phosphate containing formulation used in example 1.

EXAMPLE 3

Example 1 was repeated using the following detergent product at 2 g/l:

25	Dodecyl Benzene Sulphonic acid	16.0
	C ₁₂ -C ₁₅ Ethoxylated alcohol nonionic surfactant 7 EO	7.0
	Monoethanol amine	2.0
	Citric acid	6.5
30	Sodium xylene sulphonate	6.0
	Sodium hydroxide	4.1
	protease	0.5
	Minors and water to 100%	

The cleaning results are shown in the Table. The lipase effect in this anionic-rich detergent composition is rather small.

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EXAMPLE 4

Example 1 was repeated using the following detergent product at 3 g/l:

- | | | | | |
|----|--|---------|----|---------|
| 5 | C ₁₂ -C ₁₅ Ethoxylated alcohol nonionic surfactant | 10.5-13 | EO | |
| | | | | 9.0 |
| | Sodium sulphate | | | 36.8 |
| | Sodium carbonate | | | 38.5 |
| | Sodium silicate | | | 7.0 |
| 10 | Diatomeous Earth | | | 1.9 |
| | Sodium carboxymethyl cellulose | | | 0.1 |
| | Fluorescer | | | 0.1 |
| | Water and minors | | | to 100% |
- 15 The cleaning results are shown in the Table. It can be seen that the lipase effect in this nonionic-rich detergent composition is large.

Detergent Composition	Dosage (g/l)	Lipase Concentration (LU/ml)		Reflectance at 460nm after US wash		Lipase effect: Delta Reflec- tance	US power (Watt)
		Lipolase 30T	Lipolase 100T	+ Lipase	- Lipase		
Example 1	3.0	5.0		44.9	44.8	0.1	38.0
		15.0		43.7	42.2	1.5	17.0
		15.0		37.8	35.9	1.9	33.0
		15.0		36.8	35.3	1.5	33.0
		30.0		46.3	44.8	1.5	38.0
			15.0	48.7	44.8	3.9	38.0
Example 2	2.6		15.0	38.3	35.3	3.0	33.0
				38.8	35.0	3.8	33.0
Example 3	2.0			39.2	34.1	5.1	33.0
			15.0	29.7	29.2	0.5	33.0
Example 4	3.0			32.8	28.9	3.9	33.0
			15.0				

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EXAMPLE 5

Polyester EMPA test clothes of Example 1, soiled with 3 wt% tri-glycerol-oleate, were washed with 2 liter water comprising 4.6 g Borax. The pH of the wash liquor was adjusted to 9.2 using a HCl solution, and further the liquor had 5 FH. A US bath was used at 33 kHz, 80 Watt, at 30°C for 30 minutes. The level of H³ labelled glycerol in the wash liquor was determined and the detergency % (i.e. the percentage of the total soil that is removed after the wash) was determined for wash liquor without enzyme having lipolytic activity, for wash liquor comprising additionally 10 LU/ml lipolase and for wash liquor comprising additionally 10 LU/ml cutinase (derived from the cutinase gene from Fusarium solani pisi that is described in Ettinger et al., (1987) Biochemistry 26, 7883-7892). The following results were obtained.

lipolytic enzyme	detergency %
-	0
lipolase®	59
cutinase	85

The results show increased detergency for wash liquor comprising an enzyme having lipolytic activity. It is believed that the wash results will be even better when surface active agents are present, e.g. as regards anti-redeposition.

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CLAIMS

1. A process for cleaning articles whereby soiled articles are immersed in an enzymatic aqueous cleaning medium and radiated with ultrasonic energy, characterised in that the enzymatic aqueous cleaning medium contains an enzyme having lipolytic activity of 0.1 to 500 LU/ml.
2. Process according to claim 1, wherein the cleaning medium comprises surface active agents.
3. Process according to claims 1-2, wherein the soiled articles are selected from fabrics, dishes and other table ware.
4. Process according to claims 1-3, in which the enzyme having lipolytic activity is selected from Thermomyces lipases or variants thereof, cutinases or variants thereof, Pseudomonas lipases or variants thereof, Fusarium lipases or variants thereof and/or Chromobacter lipases or variants thereof.
5. Process according to any one of the preceding claims, in which the enzymatic aqueous cleaning medium contains 0.5 to 50 LU/ml.
6. Process according to any one of the preceding claims, in which the enzymatic aqueous cleaning medium comprises 0.05 to 50 g/l, preferably 0.1 to 5 g/l of a detergent composition.
7. Process according to any one of the preceding claims, in which the enzymatic aqueous cleaning medium comprises from 0.001 to 20 g/l of surface active agents.

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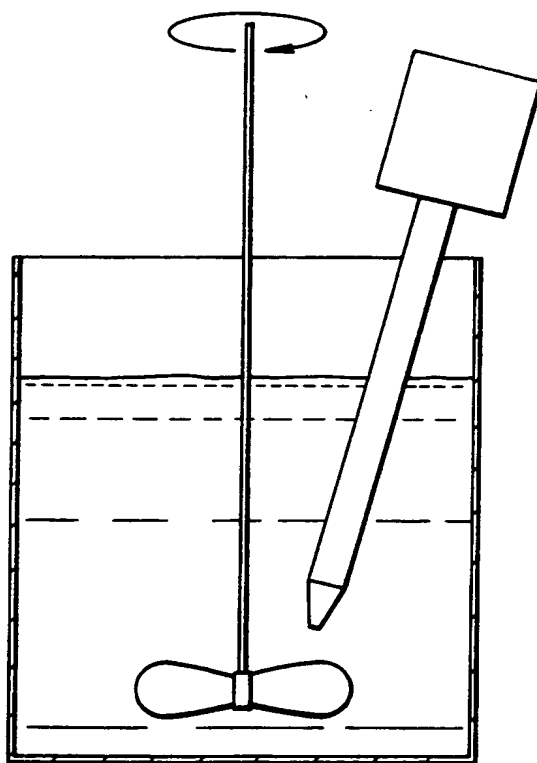
8. Process according to any one of the preceding claims, in which the enzymatic aqueous cleaning medium further comprises 0.1 to 500 GU/l of a proteolytic enzyme.

9. A process according to any one of the preceding claims, including the further step of de-aerating the aqueous cleaning medium.

10. A process according to any one of the preceding claims, wherein the ultrasonic energy is applied to the cleaning medium for 15 minutes or less.

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Fig. 1



SUBSTITUTE SHEET

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 93/02559

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C11D11/00 C11D3/386

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 320 852 (NICCO BIO TECHNICA) 21 June 1989 see column 2, line 53 - column 4, line 1 ----	1,7-9
A	EP,A,0 258 816 (HENKEL) 9 March 1988 cited in the application see page 9, line 43 - page 10, line 54; example 90 ----	1,2,10
A	WO,A,88 09367 (GENENCOR) 1 December 1988 see page 6 - page 8 ----	1,2
A	EP,A,0 399 681 (CLOROX) 28 November 1990 see page 3, line 1 - line 27; table II see page 21, line 42 - line 47; table XXI ----- -/--	1,2,5

☒ Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search

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Name and mailing address of the ISA

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INTERNATIONAL SEARCH REPORT

International Application No.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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